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(54) Titre : METHODE POUR LA METATHESE DE POLYMERES FONCTIONNALISES

(54) Title: PROCESS FOR THE METATHESIS OF FUNCTIONALIZED POLYMERS

(57) Abrégé/Abstract:

A low-molecular weight nitrite rubber having narrower molecular weight distributions than those known in the art can be prepared by olefin metathesis.



Abstract

A low-molecular weight nitrile rubber having narrower molecular weight distributions than those known in the art can be prepared by olefin metathesis.

Process for the Metathesis of Functionalized Polymers

Field of the Invention.

The present invention relates to nitrile rubber polymers having lower molecular weights and narrower molecular weight distributions than those known in the art.

Background of the Invention

Nitrile rubber (NBR), a co-polymer of a conjugated diene and an unsaturated nitrile, is a specialty rubber which has very chemical resistance, and excellent oil resistance. Coupled with the high level of mechanical properties of the rubber (in particular the high resistance to abrasion) it is not surprising that NBR has found widespread use in the automotive (seals, hoses, bearing pads), electrical (cable sheathing), mechanical engineering (wheels, rollers) and footwear industries, amongst others.

15

Commercially available NBR is manufactured by emulsion polymerization. The monomers are emulsified in water, a free radical-generating catalyst is added and the mixture is agitated whilst a constant temperature is maintained. After the desired degree of polymerization is reached, a shortstop and stabilizers are added to the reaction system causing termination of the polymerization process. Generally, NBR obtained by this process has a Mooney viscosity in the range of from about 30 to about 90, an Mw in the range of from about 250,000 to about 350,000, an Mn in the range of from about 80,000 to about 150,000 and a polydispersity index greater than about 3.2.

In addition, so-called "liquid NBR" having a very low Mooney viscosity and a low molecular weight can be produced by adding the shortstop agent early in the reaction process. As in the case of regular NBR, the resulting liquid NBR has a polydispersity greater than 3.0.

Karl Ziegler's discovery of the high effectiveness of certain metal salts, in combination with main group alkylating agents, to promote olefin polymerization under mild conditions has had a significant impact on chemical research and production to date. It was discovered early on that some "Ziegler-type" catalysts not only promote the proposed coordination-insertion mechanism but also effect an entirely different chemical process, that is the mutual exchange (or metathesis) reaction of alkenes

35



Figure 1

Acyclic diene metathesis (or ADMET) is catalyzed by a great variety of transition metal complexes as well as non-metallic systems. Heterogeneous catalyst systems based on metal oxides, sulfides or metal salts were originally used for the metathesis of olefins. However, the limited stability (especially towards hetero-substituents) and the lack of selectivity resulting from the numerous active sites and side reactions are major drawbacks of the heterogeneous systems.

Homogeneous systems have also been devised and used to effect olefin metathesis. These systems offer significant activity and control advantages over the heterogeneous catalyst systems. For example, certain Rhodium based complexes are effective catalysts for the metathesis of electron-rich olefins.

The discovery that certain metal-alkylidene complexes are capable of catalyzing the metathesis of olefins triggered the development of a new generation of well-defined, highly active, single-site catalysts. Amongst these, Bis-(tricyclohexylphosphine)-benzylidene ruthenium dichloride (commonly known as Grubb's catalyst) has been widely used, due to its remarkable insensitivity to air and moisture and high tolerance towards various functional groups. Unlike the molybdenum-based metathesis catalysts, this ruthenium carbene catalyst is stable to acids, alcohols, aldehydes and quaternary amine salts and can be used in a variety of solvents (C_6H_6 , CH_2Cl_2 , THF, *t*-BuOH). The most commonly-used catalysts are based on Mo, W and Ru.

The use of transition-metal catalyzed alkene metathesis has since enjoyed increasing attention as a synthetic method. Research efforts have been mainly focused on the synthesis of small molecules, but the application of olefin metathesis to polymer synthesis has allowed the preparation of new polymeric material with unprecedented properties (such as highly stereoregular poly-norbornadiene).

The utilization of olefin metathesis as a means to produce low molecular weight compounds from unsaturated elastomers has received growing interest. The principle for the molecular weight reduction of unsaturated polymers is shown in Figure 2. The use of an appropriate catalyst allows the cross-metathesis of the unsaturation of the polymer with the co-olefin. The end result is the cleavage of the polymer chain at the unsaturation sites and the generation of polymer fragments having lower molecular weights. In addition, another effect of this process is the "homogenizing" of the polymer chain lengths, resulting in a reduction of the polydispersity. From an application and processing stand point, a narrow molecular weight distribution of the raw polymer results in improved physical properties of the vulcanized rubber, whilst the lower molecular weight provides good processing behavior.

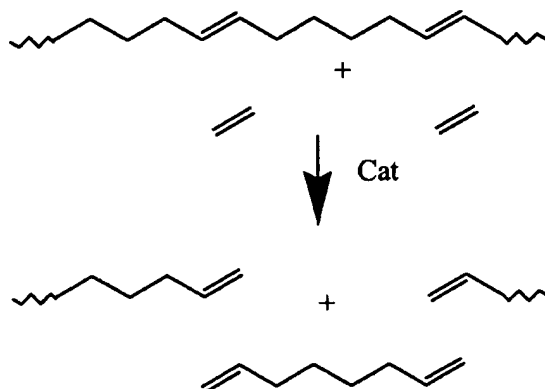


Figure 2 Metathesis of Partially Unsaturated Polymer

The so-called "depolymerization" of copolymers of 1,3-butadiene with a variety of co-monomers (styrene, propene, divinylbenzene and ethylvinylbenzene, acrylonitrile, vinyltrimethylsilane and divinyltrimethylsilane) in the presence of classical Mo and W catalyst system has been investigated. Similarly, the degradation of a nitrile rubber using WCl_6 and $SnMe_4$ or $PhC\equiv CH$ co-catalyst was reported in 1988. However, the focus of such research was to produce only low molecular fragments which could be characterized by conventional chemical means and contains no teaching with respect to the preparation of low molecular weight nitrile rubber polymers. Furthermore, such processes are non-controlled and produce a wide range of products.

The catalytic depolymerization of 1,4-polybutadiene in the presence of substituted olefins or ethylene (as chain transfer agents) in the presence of well-defined Grubb's or Schrock's catalysts is also possible. The use of Molybdenum or Tungsten compounds of the general structural formula $\{M(=NR_1)(OR_2)_2(=CHR)\}$; $M = Mo, W$ to produce low molecular weight polymers or oligomers from gelled polymers containing internal unsaturation along the polymer backbone was claimed in US 5,446,102. Again, however, the process disclosed is non-controlled, and there is no teaching with respect to the preparation of low molecular weight nitrile rubber polymers.

10 Summary of the Invention

We have now discovered that a low molecular weight nitrile rubber having narrower molecular weight distributions than those known in the art can be prepared by olefin metathesis. Rubbers having a narrow molecular weight distribution have certain advantages over those having a broad molecular weight distribution, one of these being that they have improved physical properties, resulting, for example, in better processability of the rubber.

Thus, one aspect of the disclosed invention is a nitrile rubber having a molecular weight (M_w) in the range of from about 25,000 to about 200,000, a Mooney viscosity (ML 1+4 100) of less than about 25, and a MWD (or polydispersity index) of less than about 2.5.

Description of the Invention

As used throughout this specification, the term "nitrile rubber" is intended to have a broad meaning and is meant to encompass a copolymer of a conjugated diene and an unsaturated nitrile.

The conjugated diene may be a C_4 - C_8 conjugated diene. Non-limiting examples of suitable such conjugated dienes may be selected from the group comprising butadiene, isoprene, piperylene, 2,3-dimethyl butadiene and mixtures thereof. The preferred C_4 - C_6 conjugated diene may be selected from the group comprising butadiene, isoprene and mixtures thereof. The most preferred C_4 - C_6 conjugated diene is butadiene.

The unsaturated nitrile may be a C₃-C₅ α,β-unsaturated nitrile. Non-limiting examples of suitable such C₃-C₅ α,β-unsaturated nitriles may be selected from the group comprising acrylonitrile, methacrylonitrile, thacrylonitrile and mixtures thereof. The most preferred C₃-C₅ α,β-unsaturated nitrile is acrylonitrile.

5

Preferably, the copolymer comprises from about 40 to about 85 weight percent of the copolymer of bound conjugated diene and from about 15 to about 60 weight percent of the copolymer of bound unsaturated nitrile. More preferably, the copolymer comprises from about 60 to about 75 weight percent of the copolymer of bound conjugated diene and from about 25 to about 40 weight percent of the copolymer of bound unsaturated nitrile. Most preferably, the copolymer comprises from about 60 to about 70 weight percent of the copolymer of bound conjugated diene and from about 30 to about 40 weight percent of the copolymer of bound unsaturated nitrile.

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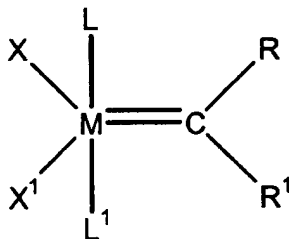
Optionally, the copolymer may further comprise a bound unsaturated carboxylic acid. Non-limiting examples of suitable such bound unsaturated carboxylic acids may be selected from the group comprising fumaric acid, maleic acid, acrylic acid, methacrylic acid and mixtures thereof. The bound unsaturated carboxylic acid may be present in an amount of from about 1 to about 10 weight percent of the copolymer, with this amount displacing a corresponding amount of the conjugated diolefin.

20

Further, a third monomer may be used in production of the nitrile polymer. Preferably, the third monomer is an unsaturated mono- or di-carboxylic acid or derivative thereof (e.g., esters, amides and the like).

25

The metathesis reaction can be catalysed by compounds of formula I, II or III; as shown below :



Formula I

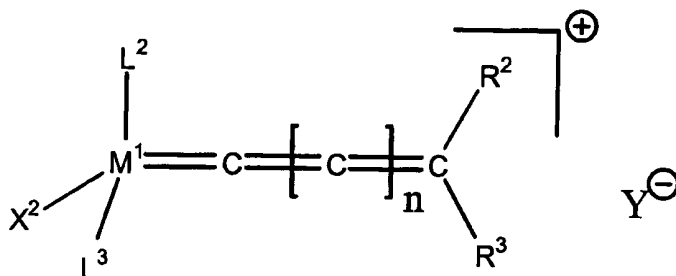
wherein:

M is Os or Ru;

R and R¹ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy carbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

X and X¹ are independently selected anionic ligands; and

L and L¹ are, independently, ligands selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines having up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxy carbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibines, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines; optionally, L and L¹ can be linked to one another to form a bidentate neutral ligand wherein at least one of the above-mentioned functional groups is present.



Formula II

wherein:

M¹ is Os or Ru;

R² and R³ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy carbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

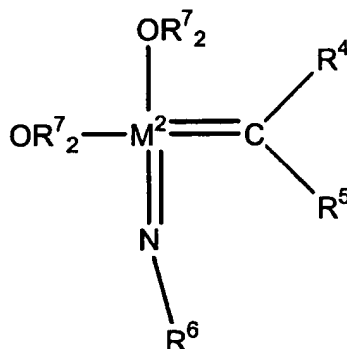
X² is selected from any anionic ligand; and

L² is a neutral π -bonded ligand, preferably but not limited to arene, substituted arene, heteroarene, independent of whether they are mono- or polycyclic;

L³ is a ligand selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines bearing up to three

aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibenes, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines;

- 5 Y⁻ is a non-coordinating anion;
 n is an integer in the range of from 0 to 5;



Formula III

wherein

- 10 M² is Mo or W
 R⁴, R⁵ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;
 15 R⁶ and R⁷ are independently selected from any unsubstituted or halo-substituted alkyl, aryl, aralkyl groups or silicon-containing analogs thereof.

- 20 Catalysts of Formula I are preferred. More preferably, catalysts of Formula I wherein L and L¹ are trialkylphosphines, X and X¹ are chloride ions and M is Ruthenium are preferred.

- 25 The amount of catalyst employed in the metathesis reaction will depend upon the nature and activity of the catalyst in question. Typically, the ratio of catalyst to NBR is in the range of from about 0.005 to about 5, preferably in the range of from about 0.025 to about 1 and, more preferably, in the range of from about 0.1 to about 0.5.

The metathesis reaction is carried out in the presence of a co-olefin. The co-olefin may be a hydrocarbon or it may be functionalised, with the caveat that it should not inactivate the metathesis catalyst or otherwise interfere with the reaction. Preferred olefins include, but are not limited to, C₂ to C₁₆ linear or branched olefins such as ethylene, isobutene, styrene or 1-hexene. Where the co-olefin is a liquid (such as 1-hexene), the amount of co-olefin employed is in the range of from about 1 to about 50 weight %; preferably in the range of from about 10 to about 30 weight %. Where the co-olefin is a gas (such as ethylene) the amount of co-olefin employed is such that it results in a pressure in the reaction vessel in the range of from about 3 to about 3600 psi, preferably in the range of from about 15 to about 1500 psi and, more preferably, in the range of from about 75 to about 600 psi.

The metathesis reaction can be carried out in any suitable solvent which does not inactivate the catalyst or otherwise interfere with the reaction. Preferred solvents include, but are not limited to, dichloromethane, benzene, toluene, tetrahydrofuran, methyl ethyl ketone, cyclohexane and the like. The most preferred solvent is monochlorobenzene (MCB). In certain cases the co-olefin can itself act as a solvent (for example, 1-hexene), in which case no other solvent is necessary.

The concentration of NBR in the reaction mixture is not critical but, obviously, should be such that the reaction is not hampered if the mixture is too viscous to be stirred efficiently, for example. Preferably, the concentration of NBR is in the range of from about 1 to about 40%, most preferably in the range of from about 6 to about 15%.

The metathesis reaction is carried out at a temperature in the range of from about 20 to about 140°C; preferably in the range of from about 60 to about 120°C.

The reaction time will depend upon a number of factors, including cement concentration, amount of catalyst used and the temperature at which the reaction is performed. The metathesis is complete within the first two hours under typical conditions. The progress of the metathesis reaction may be monitored by standard analytical techniques, for example using GPC or solution viscosity.

The Mooney viscosity of the rubber was determined using ASTM test D1646.

For a typical product the Mn is about 30,000 (compared to about 85,000 for the starting polymer) whilst the Mw is about 55,000 (compared to 300,000 for the starting polymer). As can be seen from Table 1, however, higher molecular weights (Mw) can also be obtained by manipulation of the experimental conditions (for example by lowering the catalyst loading). As expected, the molecular weight distribution falls from about 3.5 for the starting NMB feedstock to about 2.0 for the metathesized product. This is consistent with a more homogeneous range of polymer chain lengths and molecular weights.

A summary of the polymer properties for selected samples is shown in Table 1. The GPC results show up to a fivefold reduction in Mw and a narrowing of the polydispersity index to about 2.0.

Table 1 Summary of Polymer Properties

	MN	MW	MZ	PDI	Mooney Viscosity (ML 1+4 @ 100)
Starting NBR (Perbunan)	85000	296000	939000	3.50	35
Experiment 1	27000	54000	92000	2.00	2.5
Experiment 2	27000	53000	89000	1.98	-
Experiment 3	32000	66000	117000	2.06	-
Experiment 4	67000	134000	253000	2.00	-

Experimental Details

Bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (Grubb's metathesis catalyst), 1-hexene and monochlorobenzene (MCB) were purchased from Alfa, Aldrich Chemicals, and PPG respectively and used as received. Perbunan was obtained from Bayer Inc.

The metathesis reactions were carried out in a Parr high-pressure reactor under the following conditions:

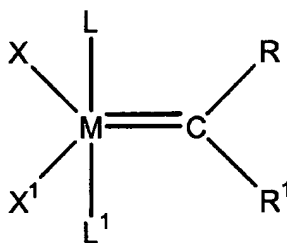
Cement Concentration 6 or 15%

	Co-Olefin	Ethylene or 1-Hexene
	Co-Olefin Concentration	Variable
	Agitator Speed	600 rpm
	Reactor Temperature	Variable
5	Catalyst Loading	Variable
	Solvent	Monochlorobenzene
	Substrate	Perbunan NT 3435 T
		Perbunan NT 3429 T

- 10 In a typical lab experiment, 200g of rubber was dissolved in 1133g of MCB (15% solid). The cement was then charged to the reactor and degassed 3 times with C_2H_4 (100 psi) under full agitation. The reactor was heated to desired temperature and 60mL of a monochlorobenzene solution containing Grubb's catalyst was added to the reactor. The temperature was maintained constant for the duration of the reaction. A cooling
- 15 coil connected to a temperature controller and a thermal sensor was used to regulate the temperature. The progress of the reaction was monitored using solution viscosity measurements for the 6% cements. At higher cement concentration, the reaction was assumed to be complete after 18 hours.

Claims

1. A process for the preparation of a nitrile rubber which comprises subjecting a nitrile rubber to metathesis in the presence of a co-olefin and a catalyst selected from the group consisting of Formula I, II and III :



Formula I

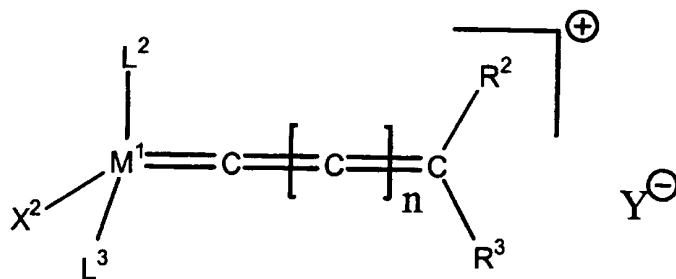
wherein:

M is Os or Ru;

- 10 R and R' are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

X and X' are independently selected anionic ligands; and

- 15 L and L' are, independently, ligands selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines having up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibines, ethers, amines, amides, imines, 20 sulfoxides, thioethers and pyridines; optionally, L and L' can be linked to one another to form a bidentate neutral ligand wherein at least one of the above-mentioned functional groups is present;



Formula II

wherein:

M¹ is Os or Ru;

R² and R³ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy carbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

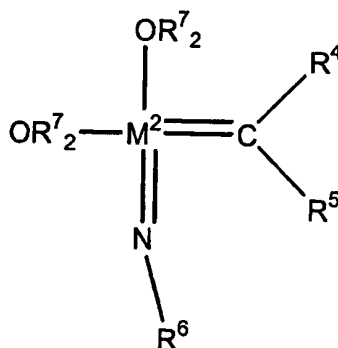
X² is selected from any anionic ligand; and

L² is a neutral π-bonded ligand, preferably but not limited to arene, substituted arene, heteroarene, independent of whether they are mono- or polycyclic;

L³ is a ligand selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines bearing up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxy carbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibenes, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines;

Y⁻ is a non-coordinating anion;

n is an integer in the range of from 0 to 5;



Formula III

wherein

M² is Mo or W

R⁴, R⁵ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy carbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

R⁶ and R⁷ are independently selected from any unsubstituted or halo-substituted alkyl, aryl, aralkyl groups or silicon-containing analogs thereof.

2. A process according to claim 1 wherein the metathesis catalyst is a compound of Formula I.

3. A process according to claim 2 wherein L and L¹ are trialkylphosphines, X and X¹ are chloride ions and M is ruthenium.

4. A process according to claim 1 wherein the ratio of catalyst to nitrile rubber is in the range of from about 0.005 to about 5.

5. A process according to claim 4 wherein the ratio of catalyst to nitrile rubber is in the range of from about 0.025 to about 1.

6. A process according to claim 5 wherein the ratio of catalyst to nitrile rubber is in the range of from about 0.1 to about 0.5.

7. A process according to claim 1 wherein the co-olefin is a C₂ to C₁₈ linear or branched olefin.

8. A process according to claim 7 wherein the co-olefin is selected from the group consisting of ethylene, isobutene, styrene and 1-hexene.

9. A process according to claim 8 wherein the co-olefin is ethylene.

10. A process according to claim 1 wherein, if the co-olefin is a liquid, the amount employed is in the range of from about 1 to about 50 weight %.

11. A process according to claim 10 wherein the amount of co-olefin employed is in the range of from about 10 to about 30 weight %.
- 5 12. A process according to claim 1 wherein, if the co-olefin is a gas, the amount employed is such that the resulting pressure in the reaction vessel is in the range of from about 3 to about 3600 psi
- 10 13. A process according to claim 12 wherein, if the co-olefin is a gas, the amount employed is such that the resulting pressure in the reaction vessel is in the range of from about 15 to about 1500 psi.
14. A process according to claim 13 wherein the amount of co-olefin employed is in the range of from about 75 to about 600 psi.
- 15 15. A process according to claim 1 wherein the process is carried out in an inert solvent selected from the group consisting of monochlorobenzene, dichloromethane, benzene, toluene, tetrahydrofuran, methyl ethyl ketone and cyclohexane.
- 20 16. A process according to claim 15 wherein the solvent is monochlorobenzene.
17. A process according to claim 1 wherein the concentration of nitrile rubber is in the range of from about 1 to about 40%.
- 25 18. A process according to claim 17 wherein the concentration of nitrile rubber is in the range of from about 6 to about 15%.
19. A process according to claim 1 wherein the metathesis reaction is carried out at a temperature in the range of from about 20 to about 140°C.
- 30 20. A process according to claim 19 wherein the metathesis reaction is carried out at a temperature in the range of from about 60 to about 120°C.



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(74) Agent: SMART & BIGGAR

(54) Titre : CAOUTCHOUC NITRILE HYDROGENE DE FAIBLE POIDS MOLECULAIRE

(54) Title: LOW MOLECULAR WEIGHT HYDROGENATED NITRILE RUBBER

(57) Abrégé/Abstract:

A hydrogenated nitrile rubber having lower molecular weights and narrower molecular weight distributions than those known in the art can be prepared by the claim metathesis of nitrile butadiene rubber, followed by hydrogenation of the resulting metathesised NBR.



Abstract

A hydrogenated nitrile rubber having lower molecular weights and narrower molecular weight distributions than those known in the art can be prepared by the olefin
5 metathesis of nitrile butadiene rubber, followed by hydrogenation of the resulting metathesised NBR.

Low Molecular Weight Hydrogenated Nitrile Rubber

Field of the Invention.

The present invention relates to hydrogenated nitrile rubber polymers having
5 lower molecular weights and narrower molecular weight distributions than those known
in the art.

Background of the Invention

Hydrogenated nitrile rubber (HNBR), prepared by the selective hydrogenation of
10 acrylonitrile-butadiene rubber (nitrile rubber, NBR), is a specialty rubber which has very
good heat resistance, excellent ozone and chemical resistance, and excellent oil
resistance. Coupled with the high level of mechanical properties of the rubber (in
particular the high resistance to abrasion) it is not surprising that HNBR has found
widespread use in the automotive (seals, hoses, bearing pads) oil (stators, well head
15 seals, valve plates), electrical (cable sheathing), mechanical engineering (wheels,
rollers) and shipbuilding (pipe seals, couplings) industries, amongst others.

Commercially available HNBR has a Mooney viscosity in the range of from about
55 to about 105, a molecular weight in the range of from about 200,000 to about
20 600,000, a polydispersity greater than 3.0 and a residual double bond (RDB) content in
the range of from about 1 to about 18% (by IR spectroscopy).

One limitation in processing HNBR is the relatively high Mooney Viscosity. In
principle, HNBR having a lower molecular weight and lower Mooney viscosity would
25 have better processability. Attempts have been made to reduce the molecular weight
of the polymer by mastication (mechanical breakdown) and by chemical means (for
example, using strong acid), but such methods have the disadvantages that they result
in the introduction of functional groups (such as carboxylic acid and ester groups) into
the polymer, and the altering of the microstructure of the polymer. This results in
30 unacceptable changes in the properties of the polymer. In addition, these types of
approaches, by their very nature, produce polymers having a broad molecular weight
distribution.

A hydrogenated nitrile rubber having a low Mooney (<55) and improved
35 processability, but which has the same microstructure as those rubbers which are

- currently available, is difficult to manufacture using current technologies. The hydrogenation of NBR to produce HNBR results in an increase in the Mooney viscosity of the raw polymer. This Mooney Increase Ratio (MIR) is generally around 2, depending upon the polymer grade, hydrogenation level and nature of the feedstock.
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Figure 1

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- 20 olefins. However, the limited stability (especially towards hetero-substituents) and the lack of selectivity resulting from the numerous active sites and side reactions are major drawbacks of the heterogeneous systems.

- Homogeneous systems have also been devised and used to effect olefin
- 25 metathesis. These systems offer significant activity and control advantages over the heterogeneous catalyst systems. For example, certain Rhodium based complexes are effective catalysts for the metathesis of electron-rich olefins.

The discovery that certain metal-alkylidene complexes are capable of catalyzing the metathesis of olefins triggered the development of a new generation of well-defined, highly active, single-site catalysts. Amongst these, Bis-(tricyclohexylphosphine)-benzylidene ruthenium dichloride (commonly known as Grubb's catalyst) has been
5 widely used, due to its remarkable insensitivity to air and moisture and high tolerance towards various functional groups. Unlike the molybdenum-based metathesis catalysts, this ruthenium carbene catalyst is stable to acids, alcohols, aldehydes and quaternary amine salts and can be used in a variety of solvents (C_6H_6 , CH_2Cl_2 , THF, *t*-BuOH). The most commonly-used catalysts are based on Mo, W and Ru.

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The use of transition-metal catalyzed alkene metathesis has since enjoyed increasing attention as a synthetic method. Research efforts have been mainly focused on the synthesis of small molecules, but the application of olefin metathesis to polymer synthesis has allowed the preparation of new polymeric material with unprecedented
15 properties (such as highly stereoregular poly-norbornadiene).

The utilization of olefin metathesis as a means to produce low molecular weight compounds from unsaturated elastomers has received growing interest. The principle for the molecular weight reduction of unsaturated polymers is shown in Figure 2. The
20 use of an appropriate catalyst allows the cross-metathesis of the unsaturation of the polymer with the co-olefin. The end result is the cleavage of the polymer chain at the unsaturation sites and the generation of polymer fragments having lower molecular weights. In addition, another effect of this process is the "homogenizing" of the polymer chain lengths, resulting in a reduction of the polydispersity. From an application and
25 processing stand point, a narrow molecular weight distribution of the raw polymer results in improved physical properties of the vulcanized rubber, whilst the lower molecular weight provides good processing behavior.

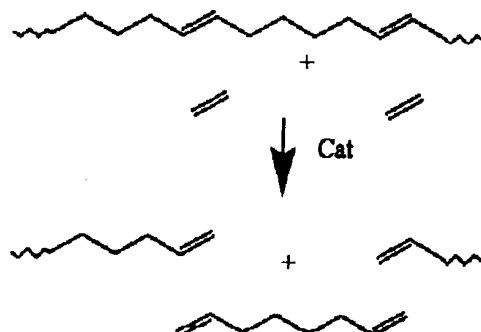


Figure 2 Metathesis of Partially Unsaturated Polymer

The so-called "depolymerization" of copolymers of 1,3-butadiene with a variety of co-monomers (styrene, propene, divinylbenzene and ethylvinylbenzene, acrylonitrile, vinyltrimethylsilane and divinyltrimethylsilane) in the presence of classical Mo and W catalyst system has been investigated. Similarly, the degradation of a nitrile rubber using WCl_6 and $SnMe_4$ or $PhC\equiv CH$ co-catalyst was reported in 1988. However, the focus of such research was to produce only low molecular fragments which could be characterized by conventional chemical means and contains no teaching with respect to the preparation of low molecular weight nitrile rubber polymers. Furthermore, such processes are non-controlled and produce a wide range of products.

The catalytic depolymerization of 1,4-polybutadiene in the presence of substituted olefins or ethylene (as chain transfer agents) in the presence of well-defined Grubb's or Schrock's catalysts is also possible. The use of Molybdenum or Tungsten compounds of the general structural formula $\{M(=NR_1)(OR_2)_2(=CHR)\}$; $M = Mo, W$ to produce low molecular weight polymers or oligomers from gelled polymers containing internal unsaturation along the polymer backbone was claimed in US 5,446,102. Again, however, the process disclosed is non-controlled, and there is no teaching with respect to the preparation of low molecular weight nitrile rubber polymers.

Summary of the Invention

We have now discovered that hydrogenated nitrile rubber having lower molecular weights and narrower molecular weight distributions than those known in the art can be

prepared by the olefin metathesis of nitrile butadiene rubber, followed by hydrogenation of the resulting metathesised NBR.

Thus, one aspect of the disclosed invention is a saturated nitrile rubber having a
5 molecular weight (M_w) in the range of from about 30,000 to about 250,000, a Mooney viscosity (ML 1+4 100) of between about 3 and about 50, and a MWD (or polydispersity index) of less than about 2.5.

Description of the Invention

10 As used throughout this specification, the term "nitrile polymer" is intended to have a broad meaning and is meant to encompass a copolymer of a conjugated diene and an unsaturated nitrile.

The conjugated diene may be a C_4 - C_6 conjugated diene. Non-limiting examples
15 of suitable such conjugated dienes may be selected from the group comprising butadiene, isoprene, piperylene, 2,3-dimethyl butadiene and mixtures thereof. The preferred C_4 - C_6 conjugated diene may be selected from the group comprising butadiene, isoprene and mixtures thereof. The most preferred C_4 - C_6 conjugated diene is butadiene.

20

The unsaturated nitrile may be a C_3 - C_6 α,β -unsaturated nitrile. Non-limiting
examples of suitable such C_3 - C_6 α,β -unsaturated nitriles may be selected from the
group comprising acrylonitrile, methacrylonitrile, ethacrylonitrile and mixtures thereof.
The most preferred C_3 - C_6 α,β -unsaturated nitrile is acrylonitrile.

25

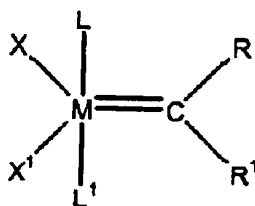
Preferably, the copolymer comprises from about 40 to about 85 weight percent
of the copolymer of bound conjugated diene and from about 15 to about 60 weight
percent of the copolymer of bound unsaturated nitrile. More preferably, the copolymer
comprises from about 60 to about 75 weight percent of the copolymer of bound
30 conjugated diene and from about 25 to about 40 weight percent of the copolymer of
bound unsaturated nitrile. Most preferably, the copolymer comprises from about 60 to
about 70 weight percent of the copolymer of bound conjugated diene and from about
30 to about 40 weight percent of the copolymer of bound unsaturated nitrile.

Optionally, the copolymer may further comprise a bound unsaturated carboxylic acid. Non-limiting examples of suitable such bound unsaturated carboxylic acids may be selected from the group comprising fumaric acid, maleic acid, acrylic acid, methacrylic acid and mixtures thereof. The bound unsaturated carboxylic acid may be present in an amount of from about 1 to about 10 weight percent of the copolymer, with this amount displacing a corresponding amount of the conjugated diolefin.

Further, a third monomer may be used in production of the nitrile polymer. Preferably, the third monomer is an unsaturated mono- or di-carboxylic acid or derivative thereof (e.g., esters, amides and the like).

Step 1: Metathesis

The metathesis reaction can be catalysed by compounds of formula I, II or III; as shown below :



Formula I

wherein:

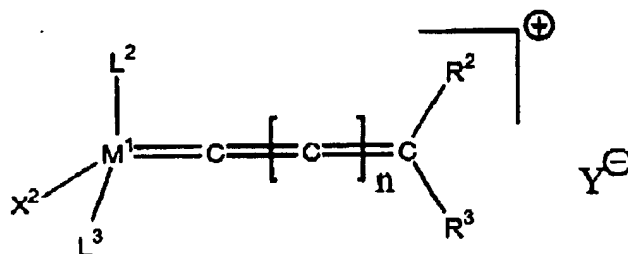
M is Os or Ru;

R and R' are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₈-C₂₀ alkenyl, C₈-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

X and X' are independently selected anionic ligands; and

L and L' are, independently, ligands selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines having up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibines, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines; optionally, L and L' can be linked to one another to

from a bidentate neutral ligand wherein at least one of the above-mentioned functional groups is present.



Formula II

5 wherein:

M¹ is Os or Ru;

R² and R³ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy-carbonyl, C₁-C₂₀

10 alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

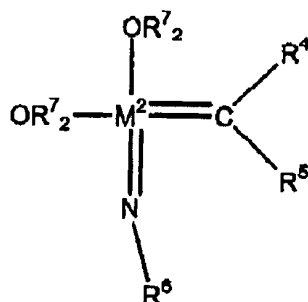
X² is selected from any anionic ligand; and

L² is a neutral π-bonded ligand, preferably but not limited to arene, substituted arene, heteroarene, independent of whether they are mono- or polycyclic;

15 L³ is a ligand selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines bearing up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibenes, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines;

20 Y⁻ is a non-coordinating anion;

n is an integer in the range of from 0 to 5;



Formula III

wherein

M^2 is Mo or W

R^4 , R^5 are, independently, hydrogen or a hydrocarbon selected from the group consisting of C_2 - C_{20} -alkenyl, C_2 - C_{20} -alkynyl, C_1 - C_{20} -alkyl, aryl, C_1 - C_{20} -carboxylate, C_1 - C_{20} ...
 5 alkoxy, C_2 - C_{20} alkenyloxy, C_2 - C_{20} alkynyloxy, aryloxy, C_2 - C_{20} alkoxycarbonyl, C_1 - C_{20} alkylthio, C_1 - C_{20} alkylsulfonyl and C_1 - C_{20} alkylsulfinyl;

R^6 and R^7 are independently selected from any unsubstituted or halo-substituted alkyl, aryl, aralkyl groups or silicon-containing analogs thereof.

10

Catalysts of Formula I are preferred. More preferably, catalysts of Formula I wherein L and L' are trialkylphosphines, X and X' are chloride ions and M is Ruthenium are preferred.

15

The amount of catalyst employed in the metathesis reaction will depend upon the nature and activity of the catalyst in question. Typically, the ratio of catalyst to NBR is in the range of from about 0.005 to about 5, preferably in the range of from about 0.025 to about 1 and, more preferably, in the range of from about 0.1 to about 0.5.

20

The metathesis reaction is carried out in the presence of a co-olefin which is a C_1 to C_{16} linear or branched olefin such as ethylene, isobutene, styrene or 1-hexene. Where the co-olefin is a liquid (such as 1-hexene), the amount of co-olefin employed is in the range of from about 1 to about 50 weight %; preferably in the range of from about 10 to about 30 weight %. Where the co-olefin is a gas (such as ethylene) the amount of
 25 co-olefin employed is such that it results in a pressure in the reaction vessel in the range of from about 15 to about 1500 psi, preferably in the range of from about 75 to about 600 psi.

The metathesis reaction can be carried out in any suitable solvent which does not inactivate the catalyst or otherwise interfere with the reaction. Preferred solvents include, but are not limited to, dichloromethane, benzene, toluene, tetrahydrofuran, cyclohexane and the like. The most preferred solvent is monochlorobenzene (MCB). In certain cases the co-olefin can itself act as a solvent (for example, 1-hexene), in which case no other solvent is necessary.

The concentration of NBR in the reaction mixture is not critical but, obviously, should be such that the reaction is not hampered if the mixture is too viscous to be stirred efficiently, for example. Preferably, the concentration of NBR is in the range of from about 1 to about 20%, most preferably in the range of from about 6 to about 15%.

The metathesis reaction is carried out at a temperature in the range of from about 20 to about 140°C; preferably in the range of from about 60 to about 120°C.

The reaction time will depend upon a number of factors, including cement concentration, amount of catalyst used and the temperature at which the reaction is performed. The metathesis is complete within the first two hours under typical conditions. The progress of the metathesis reaction may be monitored by standard analytical techniques, for example using GPC or solution viscosity.

Step 2: Hydrogenation

Reduction of the product from the metathesis reaction can be effected using standard reduction techniques known in the art. For example, homogeneous hydrogenation catalysts known to those of skill in the art, such as Wilkinson's catalyst $\{(PPh_3)_3RhCl\}$ and the like can be used.

The hydrogenation may be performed *in situ* i.e. in the same reaction vessel in which the metathesis step is carried out, without the need to first isolate the metathesised product. The hydrogenation catalyst is simply added to the vessel, which is then treated with hydrogen to produce the HNBR.

Grubb's catalyst, in the presence of hydrogen, is converted to a dihydride complex $(PR_3)_2RuCl_2H_2$, which is itself an olefin hydrogenation catalyst. Thus, in a one-pot reaction, Grubb's catalyst was used to reduce the molecular weight of NBR in the presence of co-olefin. The reaction mixture was then treated with hydrogen, converting
5 the Grubb's complex to the dihydride species which then hydrogenated the metathesis product to produce the HNBR of the invention. The rate of hydrogenation was lower in this case than in the case where Wilkinson's catalyst was used for the hydrogenation step, but it is clear that such an approach is indeed a viable one.

10 The low Mooney HNBR which forms an object of the invention can be characterized by standard techniques known in the art. For example, the molecular weight distribution of the polymer was determined by gel permeation chromatography (GPC) using a Waters 2690 Separation Module and a Waters 410 Differential Refractometer running Waters Millennium software version 3.05.01. Samples were
15 dissolved in tetrahydrofuran (THF) stabilised with 0.025% BHT. The columns used for the determination were three sequential mixed-B gel column from Polymer Labs. Reference Standards used were polystyrene standards from American Polymer Standards Corp.

20 The Mooney viscosity of the rubber was determined using ASTM test D1646.

For a typical product the Mn is about 27k (compared to 85k for the starting polymer) whilst the Mw is about 54k (compared to 296k for the starting polymer). As expected, the molecular weight distribution falls from about 3.4 for the starting
25 Perbunan NT 3435 T feedstock to about 2.0 for the metathesized product. This is consistent with a more homogeneous range of polymer chain lengths and molecular weights.

A summary of the polymer properties for selected samples is shown in

	(ML 1+4 @ 100)				
Comparative Therban	98000	320000	945000	3.27	73
Starting NBR	85000	296000	939000	3.60	
Experiment 1	73000	189000	441000	2.59	43
Experiment 2	60000	136000	277000	2.27	28
Experiment 3	31000	59000	98000	1.90	3

Experimental Details

General

5 Tris(triphenylphosphine)Rhodium Chloride (Wilkinson's hydrogenation catalyst), Bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (Grubb's metathesis catalyst), 1-hexene, triphenylphosphine (TPP) and monochlorobenzene (MCB) were purchased from JMI, Alfa, Aldrich Chemicals, Elf Atochem and PPG respectively and used as received.

10

Metathesis

The metathesis reactions were carried out in a Parr high-pressure reactor under the following conditions:

	Cement Concentration	6 or 15%
15	Co-Olefin	Ethylene or 1-Hexene
	Co-Olefin Concentration	Variable
	Agitator Speed	600 rpm
	Reactor Temperature	Variable
	Catalyst Loading (Grubb's)	Variable
20	Solvent	Monochlorobenzene
	Substrate	Perbunan NT 3435 T
		Perbunan NT 3429 T

25 In a typical lab experiment, 200g of rubber was dissolved in 1133g of MCB (15% solid). The cement was then charged to the reactor and degassed 3 times with C₂H₄ (100 psi) under full agitation. The reactor was heated to desired temperature and 60mL of a monochlorobenzene solution containing Grubb's catalyst was added to the reactor.

The temperature was maintained constant for the duration of the reaction. A cooling coil connected to a temperature controller and a thermal sensor was used to regulate the temperature. The progress of the reaction was monitored using solution viscosity measurements for the 6% cements. At higher cement concentration, the reaction was
5 assumed to be complete after 18 hours.

Hydrogenation

The hydrogenation reactions were carried out in the same reactor as the metathesis under the following conditions:

10

Cement solid concentration	12%
H ₂ (g) pressure	1200 psi
Agitator Speed	600 rpm
Reactor Temperature	138°C
15 Catalyst Loading (Wilkinson's)	0.08 phr
Triphenylphosphine	1 phr
Solvent	Monochlorobenzene

In a typical lab experiment, the cement from the metathesis reaction was
20 degassed 3 times with H₂ (100 psi) under full agitation. The temperature of the reactor was raised to 130°C and a 60mL monochlorobenzene solution containing Wilkinson's catalyst and triphenylphosphine was added to the reactor. The temperature was allowed to increase to 138°C and maintained constant for the duration of the reaction. The hydrogenation reaction was monitored by measuring the residual double bond
25 (RDB) level at various intervals using IR spectroscopy.

Alternatively, the Ruthenium metathesis catalyst can be used to hydrogenate the polymer.

Claims

1. A hydrogenated nitrile rubber having a molecular weight (M_w) in the range of from about 30,000 to about 250,000 and a polydispersity index of less than about 2.5.
- 5 2. A hydrogenated nitrile rubber according to claim 1 wherein the molecular weight (M_w) is in the range of from about 40,000 to about 220,000.
3. A hydrogenated nitrile rubber according to claim 2 wherein the molecular weight
10 (M_w) is in the range of from about 55,000 to about 190,000.
4. A hydrogenated nitrile rubber according to claim 1 wherein the polydispersity Index is less than about 2.3.
- 15 5. A hydrogenated nitrile rubber according to claim 1 wherein the polydispersity Index is less than about 2.1.
6. A hydrogenated nitrile rubber according to claim 1 wherein the rubber has a Mooney viscosity (ML 1+4 100) of less than about 55.
- 20 7. A hydrogenated nitrile rubber according to claim 5 wherein the rubber has a Mooney viscosity (ML 1+4 100) of less than about 45.
8. A hydrogenated nitrile rubber according to claim 1 wherein the rubber has a Mooney
25 viscosity (ML 1+4 100) of less than about 35.
9. A hydrogenated nitrile rubber according to claim 1 wherein the rubber has a Mooney viscosity (ML 1+4 100) of less than about 30.
- 30 10. A hydrogenated nitrile rubber according to claim 1 wherein the rubber has a Mooney viscosity (ML 1+4 100) of less than about 5.
11. A hydrogenated nitrile rubber having a Mooney viscosity (ML 1+4 100) of less than about 50.

35

12. A hydrogenated nitrile rubber according to claim 11 having a Mooney viscosity (ML 1+4 100) of less than about 45.
13. A hydrogenated nitrile rubber according to claim 12 having a Mooney viscosity (ML 1+4 100) of less than about 30.
14. A hydrogenated nitrile rubber according to claim 13 having a Mooney viscosity (ML 1+4 100) of less than about 5.
15. The use of a hydrogenated nitrile rubber according to claim 1 in the manufacture of a seal, hose, bearing pad, stator, well head seal, valve plate, cable sheathing, wheel, roller or pipe seal.



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(54) Titre : METHODE POUR PREPARER DU CAOUTCHOUC NITRILE HYDROGENE DE FAIBLE MASSE
MOLECULAIRE

(54) Title: PROCESS FOR THE PREPARATION OF LOW MOLECULAR WEIGHT HYDROGENATED NITRILE RUBBER

(57) Abrégé/Abstract:

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Abstract

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Process for the Preparation of Low Molecular Weight Hydrogenated Nitrile Rubber

Field of the Invention.

5 The present invention relates to hydrogenated nitrile rubber polymers having lower molecular weights and narrower molecular weight distributions than those known in the art.

Background of the Invention

10 Hydrogenated nitrile rubber (HNBR), prepared by the selective hydrogenation of acrylonitrile-butadiene rubber (nitrile rubber; NBR), is a specialty rubber which has very good heat resistance, excellent ozone and chemical resistance, and excellent oil resistance. Coupled with the high level of mechanical properties of the rubber (in particular the high resistance to abrasion) it is not surprising that HNBR has found
15 widespread use in the automotive (seals, hoses, bearing pads) oil (stators, well head seals, valve plates), electrical (cable sheathing), mechanical engineering (wheels, rollers) and shipbuilding (pipe seals, couplings) industries, amongst others.

 Commercially available HNBR has a Mooney viscosity in the range of from about
20 55 to about 105, a molecular weight in the range of from about 200,000 to about 500,000, a polydispersity greater than 3.0 and a residual double bond (RDB) content in the range of from about 1 to about 18% (by IR spectroscopy).

 One limitation in processing HNBR is the relatively high Mooney Viscosity. In
25 principle, HNBR having a lower molecular weight and lower Mooney viscosity would have better processability. Attempts have been made to reduce the molecular weight of the polymer by mastication (mechanical breakdown) and by chemical means (for example, using strong acid), but such methods have the disadvantages that they result in the introduction of functional groups (such as carboxylic acid and ester groups) into
30 the polymer, and the altering of the microstructure of the polymer. This results in unacceptable changes in the properties of the polymer. In addition, these types of approaches, by their very nature, produce polymers having a broad molecular weight distribution.

A hydrogenated nitrile rubber having a low Mooney (<55) and improved processability, but which has the same microstructure as those rubbers which are currently available, is difficult to manufacture using current technologies. The hydrogenation of NBR to produce HNBR results in an increase in the Mooney viscosity of the raw polymer. This Mooney Increase Ratio (MIR) is generally around 2, depending upon the polymer grade, hydrogenation level and nature of the feedstock. Furthermore, limitations associated with the production of NBR itself dictate the low viscosity range for the HNBR feedstock. Currently, one of the lowest Mooney viscosity products available is Therban VP KA 8837 (available from Bayer), which has a Mooney viscosity of about 55 (ML 1+4 @ 100°C) and a RDB of about 18%.

Karl Ziegler's discovery of the high effectiveness of certain metal salts, in combination with main group alkylating agents, to promote olefin polymerization under mild conditions has had a significant impact on chemical research and production to date. It was discovered early on that some "Ziegler-type" catalysts not only promote the proposed coordination-insertion mechanism but also effect an entirely different chemical process, that is the mutual exchange (or metathesis) reaction of alkenes.



Figure 1

Acyclic diene metathesis (or ADMET) is catalyzed by a great variety of transition metal complexes as well as non-metallic systems. Heterogeneous catalyst systems based on metal oxides, sulfides or metal salts were originally used for the metathesis of olefins. However, the limited stability (especially towards hetero-substituents) and the lack of selectivity resulting from the numerous active sites and side reactions are major drawbacks of the heterogeneous systems.

Homogeneous systems have also been devised and used to effect olefin metathesis. These systems offer significant activity and control advantages over the

heterogeneous catalyst systems. For example, certain Rhodium based complexes are effective catalysts for the metathesis of electron-rich olefins.

5 The discovery that certain metal-alkylidene complexes are capable of catalyzing the metathesis of olefins triggered the development of a new generation of well-defined, highly active, single-site catalysts. Amongst these, Bis-(tricyclohexylphosphine)-benzylidene ruthenium dichloride (commonly know as Grubb's catalyst) has been widely used, due to its remarkable insensitivity to air and moisture and high tolerance towards various functional groups. Unlike the molybdenum-based metathesis catalysts,
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20 The utilization of olefin metathesis as a means to produce low molecular weight compounds from unsaturated elastomers has received growing interest. The principle for the molecular weight reduction of unsaturated polymers is shown in Figure 2. The use of an appropriate catalyst allows the cross-metathesis of the unsaturation of the polymer with the co-olefin. The end result is the cleavage of the polymer chain at the
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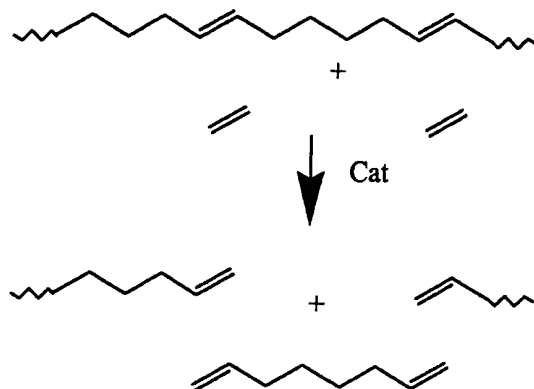


Figure 2 Metathesis of Partially Unsaturated Polymer

The so-called "depolymerization" of copolymers of 1,3-butadiene with a variety of co-monomers (styrene, propene, divinylbenzene and ethylvinylbenzene, acrylonitrile, vinyltrimethylsilane and divinyltrimethylsilane) in the presence of classical Mo and W catalyst system has been investigated. Similarly, the degradation of a nitrile rubber using WCl_6 and SnMe_4 or $\text{PhC}\equiv\text{CH}$ co-catalyst was reported in 1988. However, the focus of such research was to produce only low molecular fragments which could be characterized by conventional chemical means and contains no teaching with respect to the preparation of low molecular weight nitrile rubber polymers. Furthermore, such processes are non-controlled and produce a wide range of products.

The catalytic depolymerization of 1,4-polybutadiene in the presence of substituted olefins or ethylene (as chain transfer agents) in the presence of well-defined Grubb's or Schrock's catalysts is also possible. The use of Molybdenum or Tungsten compounds of the general structural formula $\{\text{M}(=\text{NR}_1)(\text{OR}_2)_2(=\text{CHR})\}$; $\text{M} = \text{Mo}, \text{W}\}$ to produce low molecular weight polymers or oligomers from gelled polymers containing internal unsaturation along the polymer backbone was claimed in US 5,446,102. Again, however, the process disclosed is non-controlled, and there is no teaching with respect to the preparation of low molecular weight nitrile rubber polymers.

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We have now discovered that hydrogenated nitrile rubber having lower molecular weights and narrower molecular weight distributions than those known in the art can be

prepared by the olefin metathesis of nitrile butadiene rubber, followed by hydrogenation of the resulting metathesised NBR.

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Description of the Invention

10 As used throughout this specification, the term "nitrile polymer" is intended to have a broad meaning and is meant to encompass a copolymer of a conjugated diene and an unsaturated nitrile.

The conjugated diene may be a C_4 - C_6 conjugated diene. Non-limiting examples
15 of suitable such conjugated dienes may be selected from the group comprising butadiene, isoprene, piperylene, 2,3-dimethyl butadiene and mixtures thereof. The preferred C_4 - C_6 conjugated diene may be selected from the group comprising butadiene, isoprene and mixtures thereof. The most preferred C_4 - C_6 conjugated diene is butadiene.

20 The unsaturated nitrile may be a C_3 - C_5 α,β -unsaturated nitrile. Non-limiting examples of suitable such C_3 - C_5 α,β -unsaturated nitriles may be selected from the group comprising acrylonitrile, methacrylonitrile, ethacrylonitrile and mixtures thereof. The most preferred C_3 - C_5 α,β -unsaturated nitrile is acrylonitrile.

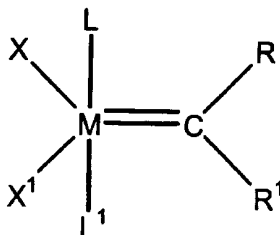
25 Preferably, the copolymer comprises from about 40 to about 85 weight percent of the copolymer of bound conjugated diene and from about 15 to about 60 weight percent of the copolymer of bound unsaturated nitrile. More preferably, the copolymer comprises from about 60 to about 75 weight percent of the copolymer of bound
30 conjugated diene and from about 25 to about 40 weight percent of the copolymer of bound unsaturated nitrile. Most preferably, the copolymer comprises from about 60 to about 70 weight percent of the copolymer of bound conjugated diene and from about 30 to about 40 weight percent of the copolymer of bound unsaturated nitrile.

Optionally, the copolymer may further comprise a bound unsaturated carboxylic acid. Non-limiting examples of suitable such bound unsaturated carboxylic acids may be selected from the group comprising fumaric acid, maleic acid, acrylic acid, methacrylic acid and mixtures thereof. The bound unsaturated carboxylic acid may be present in an amount of from about 1 to about 10 weight percent of the copolymer, with this amount displacing a corresponding amount of the conjugated diolefin.

Further, a third monomer may be used in production of the nitrile polymer. Preferably, the third monomer is an unsaturated mono- or di-carboxylic acid or derivative thereof (e.g., esters, amides and the like).

Step 1: Metathesis

The metathesis reaction can be catalysed by compounds of formula I, II or III; as shown below :



Formula I

wherein:

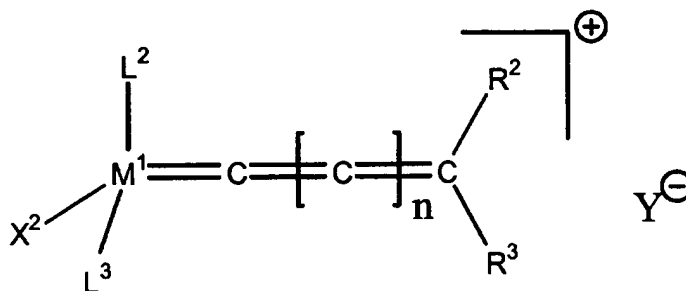
M is Os or Ru;

R and R' are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

X and X' are independently selected anionic ligands; and

L and L' are, independently, ligands selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines having up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibines, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines; optionally, L and L' can be linked to one another to

from a bidentate neutral ligand wherein at least one of the above-mentioned functional groups is present.



Formula II

5 wherein:

M¹ is Os or Ru;

R² and R³ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

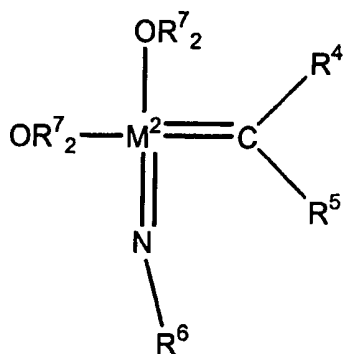
X² is selected from any anionic ligand; and

L² is a neutral π-bonded ligand, preferably but not limited to arene, substituted arene, heteroarene, independent of whether they are mono- or polycyclic;

15 L³ is a ligand selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines bearing up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibenes, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines;

20 Y⁻ is a non-coordinating anion;

n is an integer in the range of from 0 to 5;



Formula III

wherein

M^2 is Mo or W

R^4 , R^5 are, independently, hydrogen or a hydrocarbon selected from the group consisting of C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_1 - C_{20} alkyl, aryl, C_1 - C_{20} carboxylate, C_1 - C_{20} alkoxy, C_2 - C_{20} alkenyloxy, C_2 - C_{20} alkynyloxy, aryloxy, C_2 - C_{20} alkoxy carbonyl, C_1 - C_{20} alkylthio, C_1 - C_{20} alkylsulfonyl and C_1 - C_{20} alkylsulfinyl;

R^6 and R^7 are independently selected from any unsubstituted or halo-substituted alkyl, aryl, aralkyl groups or silicon-containing analogs thereof.

Catalysts of Formula I are preferred. More preferably, catalysts of Formula I wherein L and L' are trialkylphosphines, X and X' are chloride ions and M is Ruthenium are preferred.

The amount of catalyst employed in the metathesis reaction will depend upon the nature and activity of the catalyst in question. Typically, the ratio of catalyst to NBR is in the range of from about 0.005 to about 5, preferably in the range of from about 0.025 to about 1 and, more preferably, in the range of from about 0.1 to about 0.5.

The metathesis reaction is carried out in the presence of a co-olefin. The co-olefin may be a hydrocarbon or it may be functionalised, with the caveat that it should not inactivate the metathesis catalyst or otherwise interfere with the reaction. Preferred olefins include, but are not limited to, C_2 to C_{16} linear or branched olefins such as ethylene, isobutene, styrene or 1-hexene. Where the co-olefin is a liquid (such as 1-hexene), the amount of co-olefin employed is in the range of from about 1 to about 50 weight %; preferably in the range of from about 10 to about 30 weight %. Where the co-olefin is a gas (such as ethylene) the amount of co-olefin employed is such that it

results in a pressure in the reaction vessel in the range of from about 3 to about 3600 psi, preferably in the range of from about 15 to about 1500 psi and, more preferably, in the range of from about 75 to about 600 psi.

5 The metathesis reaction can be carried out in any suitable solvent which does not inactivate the catalyst or otherwise interfere with the reaction. Preferred solvents include, but are not limited to, dichloromethane, benzene, toluene, tetrahydrofuran, methyl ethyl ketone, cyclohexane and the like. The most preferred solvent is monochlorobenzene (MCB). In certain cases the co-olefin can itself act as a solvent
10 (for example, 1-hexene), in which case no other solvent is necessary.

 The concentration of NBR in the reaction mixture is not critical but, obviously, should be such that the reaction is not hampered if the mixture is too viscous to be stirred efficiently, for example. Preferably, the concentration of NBR is in the range of
15 from about 1 to about 40%, most preferably in the range of from about 6 to about 15%.

 The metathesis reaction is carried out at a temperature in the range of from about 20 to about 140°C; preferably in the range of from about 60 to about 120°C.

20 The reaction time will depend upon a number of factors, including cement concentration, amount of catalyst used and the temperature at which the reaction is performed. The metathesis is complete within the first two hours under typical conditions. The progress of the metathesis reaction may be monitored by standard analytical techniques, for example using GPC or solution viscosity .

25

Step 2: Hydrogenation

 Reduction of the product from the metathesis reaction can be effected using standard reduction techniques known in the art. For example, homogeneous
30 hydrogenation catalysts known to those of skill in the art, such as Wilkinson's catalyst $\{(PPh_3)_3RhCl\}$ and the like can be used.

 Processes for the hydrogenation of NBR are known and may also be used for the production of the hydrogenation products according to the invention. Rhodium or
35 titanium is generally used as the catalyst, although platinum, iridium, palladium,

rhenum, ruthenium, osmium, cobalt or copper in the form of the metals, but preferably in the form of metal compounds, may also be used, cf. for example US 3,700,637; DE-PS 2,539,132; EP 134 023; DE-OS 35 41 689; DE-OS 35 40 918; EP-A 298 386; DE-OS 35 29 252; DE-OS 34 33 392; US 4,464,515; and US 4,503,196.

5 Suitable catalysts and solvents for hydrogenation in homogeneous phase are described in the following, and in GB 1558491 of Bayer AG and in EP 471,250, previously incorporated herein by reference. It is not intended to restrict the catalysts and solvents for hydrogenation useful for the invention, and these are provided only by way of example.

10 The selective hydrogenation can be achieved by means of a rhodium-containing catalyst. The preferred catalyst is of the formula:



in which each R^8 is a C_1 - C_8 -alkyl group, a C_4 - C_8 -cycloalkyl group a C_6 - C_{15} -aryl group or a C_7 - C_{15} -aralkyl group, B is phosphorus, arsenic, sulfur, or a sulphoxide group $S=O$, X^3 is hydrogen or an anion, preferably a halide and more preferably a chloride or bromide ion, l is 2, 3 or 4, m is 2 or 3 and n is 1, 2 or 3, preferably 1 or 3. Preferred catalysts are tris-(triphenylphosphine)-rhodium(I)-chloride, tris(triphenylphosphine)-rhodium(III)-chloride and tris-(dimethylsulphoxide)-rhodium(III)-chloride, and tetrakis-(triphenylphosphine)-rhodium hydride of formula $((C_6H_5)_3P)_4RhH$, and the corresponding
15 compounds in which triphenylphosphine moieties are replaced by tricyclohexylphosphine moieties. The catalyst can be used in small quantities. An amount in the range of 0.01 to 1.0% preferably 0.03% to 0.5%, most preferably 0.1% to 0.3% by weight based on the weight of polymer is suitable.
20

It is known to use the catalyst with a co-catalyst that is a ligand of formula
25 $R^8_m B$, where R, m and B are as defined above, and m is preferably 3. Preferably B is phosphorus, and the R groups can be the same or different. Thus there can be used a triaryl, trialkyl, tricycloalkyl, diaryl monoalkyl, dialkyl monoaryl diaryl monocycloalkyl, dialkyl monocycloalkyl, dicycloalkyl monoaryl or dicycloalkyl monoaryl co-catalysts. Examples of co-catalyst ligands are given in US Patent No 4,631,315, the disclosure of which is incorporated by reference. The preferred co-catalyst ligand is
30 triphenylphosphine. The co-catalyst ligand is preferably used in an amount in the range 0.3 to 5%, more preferably 0.5 to 4% by weight, based on the weight of the copolymer.

Preferably also the weight ratio of the rhodium-containing catalyst compound to co-catalyst is in the range 1:3 to 1:55, more preferably in the range 1:5 to 1:45. The weight of the co-catalyst, based on the weight of one hundred parts of rubber, is suitably in the range 0.1 to 33, more suitably 0.5 to 20 and preferably 1 to 5, most preferably greater than 2 to less than 5.

The hydrogenation may be performed *in situ* i.e. in the same reaction vessel in which the metathesis step is carried out, without the need to first isolate the metathesised product. The hydrogenation catalyst is simply added to the vessel, which is then treated with hydrogen to produce the HNBR.

10

Grubb's catalyst, in the presence of hydrogen, is converted to a dihydride complex $(PR_3)_2RuCl_2H_2$, which is itself an olefin hydrogenation catalyst. Thus, in a one-pot reaction, Grubb's catalyst was used to reduce the molecular weight of NBR in the presence of co-olefin. The reaction mixture was then treated with hydrogen, converting the Grubb's complex to the dihydride species which then hydrogenated the metathesis product to produce the HNBR of the invention. The rate of hydrogenation was lower in this case than in the case where Wilkinson's catalyst was used for the hydrogenation step, but it is clear that such an approach is indeed a viable one.

20

The low Mooney HNBR which forms an object of the invention can be characterized by standard techniques known in the art. For example, the molecular weight distribution of the polymer was determined by gel permeation chromatography (GPC) using a Waters 2690 Separation Module and a Waters 410 Differential Refractometer running Waters Millenium software version 3.05.01. Samples were dissolved in tetrahydrofuran (THF) stabilised with 0.025% BHT. The columns used for the determination were three sequential mixed-B gel column from Polymer Labs. Reference Standards used were polystyrene standards from American Polymer Standards Corp.

30

The Mooney viscosity of the rubber was determined using ASTM test D1646.

For a typical product the Mn is about 27k (compared to 85k for the starting polymer) whilst the Mw is about 54k (compared to 296k for the starting polymer). As expected, the molecular weight distribution falls from about 3.4 for the starting

Perbunan NT 3435 T feedstock to about 2.0 for the metathesized product. This is consistent with a more homogeneous range of polymer chain lengths and molecular weights.

- 5 A summary of the polymer properties for selected samples is shown in Table 1. The GPC results show up to a fivefold reduction in Mw and a narrowing of the polydispersity index to a minimum of about 1.90.

Table 1 Summary of Polymer Properties

	MN	MW	MZ	PDI	Mooney Viscosity (ML 1+4 @ 100)
Comparative Therban	98000	320000	945000	3.27	73
Starting NBR	85000	296000	939000	3.50	
Experiment 1	73000	189000	441000	2.59	43
Experiment 2	60000	136000	277000	2.27	28
Experiment 3	31000	59000	98000	1.90	3

10

Experimental Details

General

- 15 Tris(triphenylphosphine)Rhodium Chloride (Wilkinson's hydrogenation catalyst), Bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (Grubb's metathesis catalyst), 1-hexene, triphenylphosphine (TPP) and monochlorobenzene (MCB) were purchased from JMI, Alfa, Aldrich Chemicals, Elf Atochem and PPG respectively and used as received.

20 *Metathesis*

The metathesis reactions were carried out in a Parr high-pressure reactor under the following conditions:

- | | |
|----------------------------|----------------------|
| Cement Concentration | 6 or 15% |
| Co-Olefin | Ethylene or 1-Hexene |
| 25 Co-Olefin Concentration | Variable |
| Agitator Speed | 600 rpm |

Reactor Temperature	Variable
Catalyst Loading (Grubb's)	Variable
Solvent	Monochlorobenzene
Substrate	Perbunan NT 3435 T
	Perbunan NT 3429 T

5

In a typical lab experiment, 200g of rubber was dissolved in 1133g of MCB (15% solid). The cement was then charged to the reactor and degassed 3 times with C_2H_4 (100 psi) under full agitation. The reactor was heated to desired temperature and 60mL of a monochlorobenzene solution containing Grubb's catalyst was added to the reactor. The temperature was maintained constant for the duration of the reaction. A cooling coil connected to a temperature controller and a thermal sensor was used to regulate the temperature. The progress of the reaction was monitored using solution viscosity measurements for the 6% cements. At higher cement concentration, the reaction was assumed to be complete after 18 hours.

15

Hydrogenation

The hydrogenation reactions were carried out in the same reactor as the metathesis under the following conditions:

20

Cement solid concentration	12%
$H_2(g)$ pressure	1200 psi
Agitator Speed	600 rpm
Reactor Temperature	138°C
Catalyst Loading (Wilkinson's)	0.08 phr
Triphenylphosphine	1 phr
Solvent	Monochlorobenzene

25

In a typical lab experiment, the cement from the metathesis reaction was degassed 3 times with H_2 (100 psi) under full agitation. The temperature of the reactor was raised to 130°C and a 60mL monochlorobenzene solution containing Wilkinson's catalyst and triphenylphosphine was added to the reactor. The temperature was allowed to increase to 138°C and maintained constant for the duration of the reaction. The hydrogenation reaction was monitored by measuring the residual double bond (RDB) level at various intervals using IR spectroscopy.

35

Alternatively, the Ruthenium metathesis catalyst can be used to hydrogenate the polymer. In such an *in situ* process the metathesis catalyst, upon treatment with hydrogen, is converted to a compound which can act as a hydrogenation catalyst.

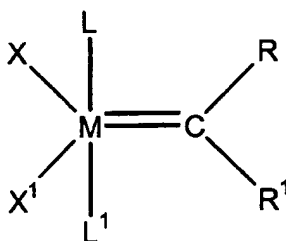
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Claims

1. A process for the preparation of a hydrogenated nitrile rubber comprising the steps of :

5

- a) subjecting a nitrile rubber to metathesis in the presence of a co-olefin and a catalyst selected from the group consisting of Formula I, II and III



Formula I

10 wherein:

M is Os or Ru;

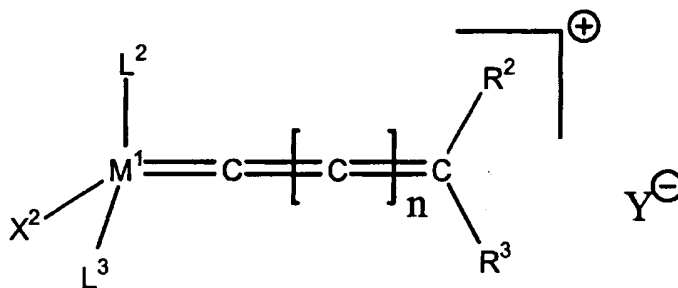
R and R' are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

15

X and X' are independently selected anionic ligands; and

L and L' are, independently, ligands selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines having up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, 20 phosphonites, phosphinamines, arsines, stibines, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines; optionally, L and L' can be linked to one another to form a bidentate neutral ligand wherein at least one of the above-mentioned functional groups is present ;

25



Formula II

wherein:

M¹ is Os or Ru;

R² and R³ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

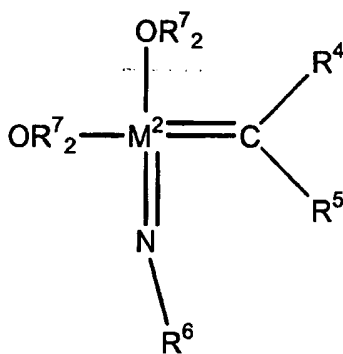
X² is selected from any anionic ligand; and

L² is a neutral π-bonded ligand, preferably but not limited to arene, substituted arene, heteroarene, independent of whether they are mono- or polycyclic;

L³ is a ligand selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines bearing up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibenes, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines;

Y⁻ is a non-coordinating anion;

n is an integer in the range of from 0 to 5;



Formula III

wherein

M² is Mo or W

R⁴, R⁵ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy carbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

R⁶ and R⁷ are independently selected from any unsubstituted or halo-substituted alkyl, aryl, aralkyl groups or silicon-containing analogs thereof.

10 and

b) hydrogenating the product of the metathesis reaction.

2. A process according to claim 1 wherein the hydrogenation is performed under homogeneous catalytic conditions.

3. A process according to claim 2 wherein the homogeneous catalytic reduction is carried out *in situ*; that is, without first isolating the product of step a).

4. A process according to claim 1 wherein the compound selected from the group consisting of Formula I, II and III can act as both a metathesis catalyst and a hydrogenation catalyst precursor.

5. A process according to claim 1 wherein the metathesis catalyst is a compound of Formula I.

6. A process according to claim 5 wherein L and L' are trialkylphosphines, X and X' are chloride ions and M is ruthenium.

7. A process according to claim 1 wherein the ratio of catalyst to nitrile rubber is in the range of from about 0.005 to about 5.

8. A process according to claim 7 wherein the ratio of catalyst to nitrile rubber is in the range of from about 0.025 to about 1.

35

9. A process according to claim 8 wherein the ratio of catalyst to nitrile rubber is in the range of from about 0.1 to about 0.5.
- 5 10. A process according to claim 1 wherein the co-olefin is a C₂ to C₁₆ linear or branched olefin.
11. A process according to claim 10 wherein the co-olefin is selected from the group consisting of ethylene, isobutene, styrene and 1-hexene.
- 10 12. A process according to claim 11 wherein the co-olefin is ethylene.
13. A process according to claim 1 wherein, if the co-olefin is a liquid, the amount employed is in the range of from about 1 to about 50 weight %.
- 15 14. A process according to claim 13 wherein the amount of co-olefin employed is in the range of from about 10 to about 30 weight %
- 20 15. A process according to claim 1 wherein, if the co-olefin is a gas, the amount employed is such that the resulting pressure in the reaction vessel is in the range of from about 3 to about 3600 psi.
- 25 16. A process according to claim 15 wherein, if the co-olefin is a gas, the amount employed is such that the resulting pressure in the reaction vessel is in the range of from about 15 to about 1500 psi.
- 30 17. A process according to claim 16 wherein the amount of co-olefin employed is in the range of from about 75 to about 600 psi.
18. A process according to claim 1 wherein the process is carried out in an inert solvent selected from the group consisting of monochlorobenzene, dichloromethane, benzene, toluene, tetrahydrofuran and cyclohexane.
19. A process according to claim 18 wherein the solvent is monochlorobenzene.

20. A process according to claim 1 wherein the concentration of nitrile rubber is in the range of from about 1 to about 20%.

21. A process according to claim 20 wherein the concentration of nitrile rubber is in the
5 range of from about 6 to about 15%.

22. A process according to claim 1 wherein the metathesis reaction is carried out at a temperature in the range of from about 20 to about 140°C.

10 23. A process according to claim 22 wherein the metathesis reaction is carried out at a temperature in the range of from about 60 to about 120°C.

24. A process according to claim 2 wherein the hydrogenation is carried out using a catalyst of formula :

15
$$(R^8_m B)_l RhX^3_n$$

wherein each R^8 is independently selected from the group consisting of a C_1 - C_8 -alkyl group, a C_4 - C_8 -cycloalkyl group, a C_6 - C_{15} -aryl group and a C_7 - C_{15} -aralkyl group;

B is selected from the group consisting of phosphorus, arsenic, sulfur, and a sulfoxide group ($S=O$) ;

20 X^3 is selected from the group consisting of hydrogen and an anion; and

l is 2, 3 or 4, m is 2 or 3 and n is 1, 2 or 3.

25. A process according to claim 24 wherein the hydrogenation catalyst is $(PPh_3)_3RhCl$.



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(54) Titre : CAOUTCHOUC NITRILE DE BAS POIDS MOLECULAIRE

(54) Title: LOW MOLECULAR WEIGHT NITRILE RUBBER

(57) Abrégé/Abstract:

A low-molecular weight nitrile rubber having narrower molecular weight distributions than those known in the art can be prepared by olefin metathesis.



Abstract

A low-molecular weight nitrile rubber having narrower molecular weight distributions than those known in the art can be prepared by olefin metathesis.

Low Molecular Weight Nitrile Rubber

Field of the Invention.

The present invention relates to nitrile rubber polymers having lower molecular weights and narrower molecular weight distributions than those known in the art.

Background of the Invention

Nitrile rubber (NBR), a co-polymer of a conjugated diene and an unsaturated nitrile, is a specialty rubber which has very chemical resistance, and excellent oil resistance. Coupled with the high level of mechanical properties of the rubber (in particular the high resistance to abrasion) it is not surprising that NBR has found widespread use in the automotive (seals, hoses, bearing pads), electrical (cable sheathing), mechanical engineering (wheels, rollers) and footwear industries, amongst others.

15

Commercially available NBR is manufactured by emulsion polymerization. The monomers are emulsified in water, a free radical-generating catalyst is added and the mixture is agitated whilst a constant temperature is maintained. After the desired degree of polymerization is reached, a shortstop and stabilizers are added to the reaction system causing termination of the polymerization process. Generally, NBR obtained by this process has a Mooney viscosity in the range of from about 30 to about 90, an Mw in the range of from about 250,000 to about 350,000, an Mn in the range of from about 80,000 to about 150,000 and a polydispersity index greater than about 3.2.

25

In addition, so-called "liquid NBR" having a very low Mooney viscosity and a low molecular weight can be produced by adding the shortstop agent early in the reaction process. As in the case of regular NBR, the resulting liquid NBR has a polydispersity greater than 3.0.

30

Karl Ziegler's discovery of the high effectiveness of certain metal salts, in combination with main group alkylating agents, to promote olefin polymerization under mild conditions has had a significant impact on chemical research and production to date. It was discovered early on that some "Ziegler-type" catalysts not only promote the

proposed coordination-insertion mechanism but also effect an entirely different chemical process, that is the mutual xchange (or metathesis) reaction of alkenes



Figure 1

Acyclic diene metathesis (or ADMET) is catalyzed by a great variety of transition metal complexes as well as non-metallic systems. Heterogeneous catalyst systems based on metal oxides, sulfides or metal salts were originally used for the metathesis of olefins. However, the limited stability (especially towards hetero-substituents) and the lack of selectivity resulting from the numerous active sites and side reactions are major drawbacks of the heterogeneous systems.

10

Homogeneous systems have also been devised and used to effect olefin metathesis. These systems offer significant activity and control advantages over the heterogeneous catalyst systems. For example, certain Rhodium based complexes are effective catalysts for the metathesis of electron-rich olefins.

15

The discovery that certain metal-alkylidene complexes are capable of catalyzing the metathesis of olefins triggered the development of a new generation of well-defined, highly active, single-site catalysts. Amongst these, Bis-(tricyclohexylphosphine)-benzylidene ruthenium dichloride (commonly known as Grubb's catalyst) has been widely used, due to its remarkable insensitivity to air and moisture and high tolerance towards various functional groups. Unlike the molybdenum-based metathesis catalysts, this ruthenium carbene catalyst is stable to acids, alcohols, aldehydes and quaternary amine salts and can be used in a variety of solvents (C_6H_6 , CH_2Cl_2 , THF, $t\text{-BuOH}$). The most commonly-used catalysts are based on Mo, W and Ru.

20

The use of transition-metal catalyzed alkene metathesis has since enjoyed increasing attention as a synthetic method. Research efforts have been mainly focused on the synthesis of small molecules, but the application of olefin metathesis to polymer

synthesis has allowed the preparation of new polymeric material with unprecedented properties (such as highly stereoregular poly-norbornadiene).

The utilization of olefin metathesis as a means to produce low molecular weight compounds from unsaturated elastomers has received growing interest. The principle for the molecular weight reduction of unsaturated polymers is shown in Figure 2. The use of an appropriate catalyst allows the cross-metathesis of the unsaturation of the polymer with the co-olefin. The end result is the cleavage of the polymer chain at the unsaturation sites and the generation of polymer fragments having lower molecular weights. In addition, another effect of this process is the "homogenizing" of the polymer chain lengths, resulting in a reduction of the polydispersity. From an application and processing stand point, a narrow molecular weight distribution of the raw polymer results in improved physical properties of the vulcanized rubber, whilst the lower molecular weight provides good processing behavior.

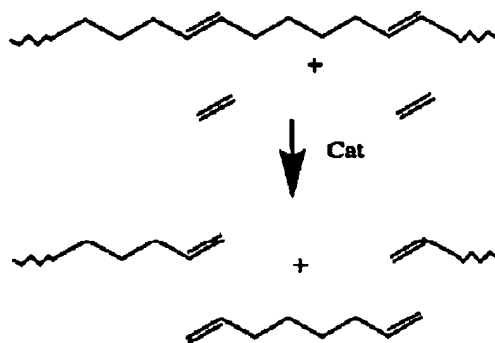


Figure-2 Metathesis of Partially Unsaturated Polymer

The so-called "depolymerization" of copolymers of 1,3-butadiene with a variety of co-monomers (styrene, propene, divinylbenzene and ethylvinylbenzene, acrylonitrile, vinyltrimethylsilane and divinylidimethylsilane) in the presence of classical Mo and W catalyst system has been investigated. Similarly, the degradation of a nitrile rubber using WCl_6 and SnMe_4 or $\text{PhC}\equiv\text{CH}$ co-catalyst was reported in 1988. However, the focus of such research was to produce only low molecular fragments which could be characterized by conventional chemical means and contains no teaching with respect to

the preparation of low molecular weight nitrile rubber polymers. Furthermore, such processes are non-controlled and produce a wide range of products.

5 The catalytic depolymerization of 1,4-polybutadiene in the presence of substituted olefins or ethylene (as chain transfer agents) in the presence of well-defined Grubb's or Schrock's catalysts is also possible. The use of Molybdenum or Tungsten compounds of the general structural formula $(M(=NR_1)(OR_2)_2(=CHR))$; $M = Mo, W$ to produce low molecular weight polymers or oligomers from gelled polymers containing internal unsaturation along the polymer backbone was claimed in US-5,446,102. Again, 10 however, the process disclosed is non-controlled, and there is no teaching with respect to the preparation of low molecular weight nitrile rubber polymers.

Summary of the Invention

15 We have now discovered that a low molecular weight nitrile rubber having narrower molecular weight distributions than those known in the art can be prepared by olefin metathesis. Rubbers having a narrow molecular weight distribution have certain advantages over those having a broad molecular weight distribution, one of these being that they have improved physical properties, resulting, for example, in better processability of the rubber.

20

Thus, one aspect of the disclosed invention is a nitrile rubber having a molecular weight (M_w) in the range of from about 25,000 to about 200,000, a Mooney viscosity (ML 1+4 100) of less than about 25, and a MWD (or polydispersity index) of less than about 2.5.

25

Description of the Invention

As used throughout this specification, the term "nitrile rubber" is intended to have a broad meaning and is meant to encompass a copolymer of a conjugated diene and an unsaturated nitrile.

30

The conjugated diene may be a C_4 - C_6 conjugated diene. Non-limiting examples of suitable such conjugated dienes may be selected from the group comprising butadiene, isoprene, piperylene, 2,3-dimethyl butadiene and mixtures thereof. The preferred C_4 - C_6 conjugated diene may be selected from the group comprising

butadiene, isoprene and mixtures thereof. The most preferred C_4-C_6 conjugated diene is butadiene.

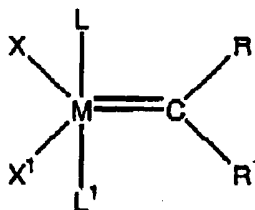
The unsaturated nitrile may be a C_3-C_5 α,β -unsaturated nitrile. Non-limiting
5 examples of suitable such C_3-C_5 α,β -unsaturated nitriles may be selected from the group comprising acrylonitrile, methacrylonitrile, ethacrylonitrile and mixtures thereof. The most preferred C_3-C_5 α,β -unsaturated nitrile is acrylonitrile.

Preferably, the copolymer comprises from about 40 to about 85 weight percent
10 of the copolymer of bound conjugated diene and from about 15 to about 60 weight percent of the copolymer of bound unsaturated nitrile. More preferably, the copolymer comprises from about 60 to about 75 weight percent of the copolymer of bound conjugated diene and from about 25 to about 40 weight percent of the copolymer of bound unsaturated nitrile. Most preferably, the copolymer comprises from about 60 to
15 about 70 weight percent of the copolymer of bound conjugated diene and from about 30 to about 40 weight percent of the copolymer of bound unsaturated nitrile.

Optionally, the copolymer may further comprise a bound unsaturated carboxylic acid. Non-limiting examples of suitable such bound unsaturated carboxylic acids may
20 be selected from the group comprising fumaric acid, maleic acid, acrylic acid, methacrylic acid and mixtures thereof. The bound unsaturated carboxylic acid may be present in an amount of from about 1 to about 10 weight percent of the copolymer, with this amount displacing a corresponding amount of the conjugated diolefin.

25 Further, a third monomer may be used in production of the nitrile polymer. Preferably, the third monomer is an unsaturated mono- or di-carboxylic acid or derivative thereof (e.g., esters, amides and the like).

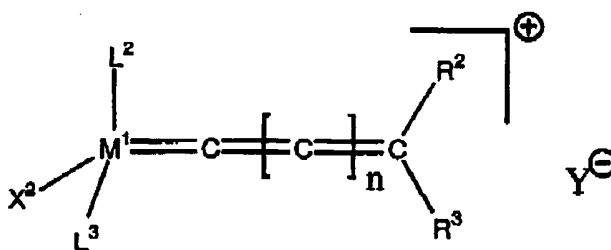
The metathesis reaction can be catalysed by compounds of formula I, II or III; as
30 shown below :



wherein:

R and R¹ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfiny;

L and L¹ are, independently, ligands selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines having up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxy-carbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibines, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines; optionally, L and L¹ can be linked to one another to form a bidentate neutral ligand wherein at least one of the above-mentioned functional groups is present.



Formula II

wherein:

20 M^1 is Os or Ru;

R² and R³ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-

C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy carbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

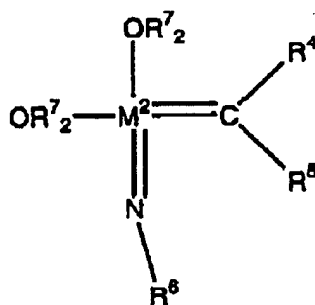
X² is selected from any anionic ligand; and

L² is a neutral π -bonded ligand, preferably but not limited to arene, substituted arene, heteroarene, independent of whether they are mono- or polycyclic;

L³ is a ligand selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines bearing up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxy carbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibenes, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines;

Y is a non-coordinating anion;

n is an integer in the range of from 0 to 5;



Formula III

15

wherein

M² is Mo or W

R⁴, R⁵ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy carbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

R⁶ and R⁷ are independently selected from any unsubstituted or halo-substituted alkyl, aryl, aralkyl groups or silicon-containing analogs thereof.

25

Catalysts of Formula I are preferred. More preferably, catalysts of Formula I wherein L and L¹ are trialkylphosphines, X and X¹ are chloride ions and M is Ruthenium are preferred.

The amount of catalyst employed in the metathesis reaction will depend upon the nature and activity of the catalyst in question. Typically, the ratio of catalyst to NBR is in the range of from about 0.005 to about 5, preferably in the range of from about 0.025 to about 1 and, more preferably, in the range of from about 0.1 to about 0.5.

The metathesis reaction is carried out in the presence of a co-olefin which is a C₁ to C₁₀ linear or branched olefin such as ethylene, isobutene, styrene or 1-hexene. Where the co-olefin is a liquid (such as 1-hexene), the amount of co-olefin employed is in the range of from about 1 to about 50 weight %; preferably in the range of from about 10 to about 30 weight %. Where the co-olefin is a gas (such as ethylene) the amount of co-olefin employed is such that it results in a pressure in the reaction vessel in the range of from about 15 to about 1500 psi, preferably in the range of from about 75 to about 600 psi.

The metathesis reaction can be carried out in any suitable solvent which does not inactivate the catalyst or otherwise interfere with the reaction. Preferred solvents include, but are not limited to, dichloromethane, benzene, toluene, tetrahydrofuran, cyclohexane and the like. The most preferred solvent is monochlorobenzene (MCB). In certain cases the co-olefin can itself act as a solvent (for example, 1-hexene), in which case no other solvent is necessary.

The concentration of NBR in the reaction mixture is not critical but, obviously, should be such that the reaction is not hampered if the mixture is too viscous to be stirred efficiently, for example. Preferably, the concentration of NBR is in the range of from about 1 to about 20%, most preferably in the range of from about 6 to about 15%.

The metathesis reaction is carried out at a temperature in the range of from about 20 to about 140°C; preferably in the range of from about 60 to about 120°C.

The reaction time will depend upon a number of factors, including cement concentration, amount of catalyst used and the temperature at which the reaction is performed. The metathesis is complete within the first two hours under typical conditions. The progress of the metathesis reaction may be monitored by standard analytical techniques, for example using GPC or solution viscosity.

The Mooney viscosity of the rubber was determined using ASTM test D1646.

For a typical product the Mn is about 30,000 (compared to about 85,000 for the starting polymer) whilst the Mw is about 55,000 (compared to 300,000 for the starting polymer). As can be seen from Table 1, however, higher molecular weights (Mw) can also be obtained by manipulation of the experimental conditions (for example by lowering the catalyst loading). As expected, the molecular weight distribution falls from about 3.5 for the starting NMB feedstock to about 2.0 for the metathesized product. This is consistent with a more homogeneous range of polymer chain lengths and molecular weights.

A summary of the polymer properties for selected samples is shown in Table 1. The GPC results show up to a fivefold reduction in Mw and a narrowing of the polydispersity Index to about 2.0.

Table 1 Summary of Polymer Properties

	MN	MW	MZ	PDI	Mooney Viscosity (ML 1+4 @ 100)
Starting NBR (Perbunan)	85000	298000	939000	3.50	35
Experiment 1	27000	54000	92000	2.00	2.5
Experiment 2	27000	53000	89000	1.98	-
Experiment 3	32000	66000	117000	2.06	-
Experiment 4	67000	134000	253000	2.00	-

Experimental Details

Bis(triisobutylphosphine)benzylidene ruthenium dichloride (Grubb's metathesis catalyst), 1-hexene and monochlorobenzene (MCB) were purchased from Alfa, Aldrich Chemicals, and PPG respectively and used as received. Perbunan was obtained from Bayer Inc.

The metathesis reactions were carried out in a Parr high-pressure reactor under the following conditions:

	Cement Concentration	6 or 15%
	Co-Olefin	Ethylene or 1-Hexene
5	Co-Olefin Concentration	Variable
	Agitator Speed	600 rpm
	Reactor Temperature	Variable
	Catalyst Loading	Variable
	Solvent	Monochlorobenzene
10	Substrate	Perbunan NT 3435 T
		Perbunan NT 3429 T

In a typical lab experiment, 200g of rubber was dissolved in 1133g of MCB (15% solid). The cement was then charged to the reactor and degassed 3 times with C_2H_4 (100 psi) under full agitation. The reactor was heated to desired temperature and 60mL of a monochlorobenzene solution containing Grubb's catalyst was added to the reactor. The temperature was maintained constant for the duration of the reaction. A cooling coil connected to a temperature controller and a thermal sensor was used to regulate the temperature. The progress of the reaction was monitored using solution viscosity measurements for the 6% cements. At higher cement concentration, the reaction was assumed to be complete after 18 hours.

Claims

1. A nitrile rubber having a molecular weight (M_w) in the range of from about 25,000 to about 200,000 and a polydispersity index of less than about 2.5.
- 5 2. A nitrile rubber according to claim 1 wherein the molecular weight (M_w) is in the range of from about 40,000 to about 180,000.
3. A nitrile rubber according to claim 1 wherein the molecular weight (M_w) is in the
10 range of from about 50,000 to about 180,000.
4. A nitrile rubber according to claim 1 wherein the polydispersity index is less than about 2.3.
- 15 5. A nitrile rubber according to claim 2 wherein the polydispersity index is less than about 2.3.
6. A nitrile rubber according to claim 3 wherein the polydispersity index is less than about 2.3.
- 20 7. A nitrile rubber according to claim 1 wherein the polydispersity index is less than about 2.1.
8. A nitrile rubber according to claim 3 wherein the polydispersity index is less than
25 about 2.1.
9. A nitrile rubber according to claim 3 wherein the polydispersity index is less than about 2.1.
- 30 10. The use of a nitrile rubber according to claim 1 in the manufacture of a seal, hose, bearing pad, stator, well head seal, valve plate, cable sheathing, wheel, roller, pipe seal or footwear component.

